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Atmospheric Chemistry and Physics Discussions

Photo-degradation of atmospheric chromophores: type conversion and changes in photochemical reactivity

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Abstract: Atmospheric chromophoric organic matters (COM) can participate in photochemical reactions because of the photosensitiveness, thus COM have a potential contribution to aerosols aging. The photochemical mechanism of atmospheric COM and the effect of photo-degradation on its photochemical reactivity are not fully understood. To address this knowledge gap, the characteristics of COM photo-degradation and the potential effects of COM photolysis on the photochemical reactivity are illustrated. COM are identified by excitation-emission matrices combined with parallel factor analysis. We confirm that both water-soluble and water-insoluble COM are photo-bleached, and an average 70% of fluorescence intensities are lost after 7 days of light exposure. Furtherly, it is found that there is a transformation process of low oxidation to high oxidation HULIS. We propose that the high oxidation HULIS could be used to trace the aging degree of aerosols. In terms of photochemical reactivity, compared with before photolysis, the triplet state COM (^{3}COM*) decrease slightly in ambient particle matter (ambient PM) samples and increase in primary organic aerosol (POA). However, the COM induce fewer singlet oxygen after photolysis. The photolysis and conversion of COM are the major cause of the change of photochemical activity. The result also enunciate that the photochemical reaction mechanisms and aerosol aging processes are relatively different in various aerosols. In conclusion, we demonstrated that the photo-degradation of COM not only change the chemical compositions, but also change the roles of the COM in the aerosol aging process.

Key word: atmospheric chromophores; photo-degradation; EEMs; triplet state; reactive oxygen species.

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1. Introduction

Chromophoric organic matters (COM) widely exist in the atmospheric environment. COM are mainly derived from biomass combustion emissions and secondary chemistry reactions (Andreae and Gelencser, 2006; Graber and Rudich, 2005; Zappoli et al., 1999). Because of the significant absorption for short wave radiation (the range of near-ultraviolet light to visible light) (Rosario-Ortiz and Canonica, 2016; Cheng et al., 2016), COM may have a significant effect on the atmospheric composition through photolysis, photo-conversion and inducing reactive substances (Chen et al., 2018; Wenk et al., 2011; Maizel et al., 2017). Simulation and evaluation of COM photochemistry improve understanding the mechanism of the aerosol aging.

As photosensitive substances in aerosol, the physical and chemical characteristics of COM change significantly under sunlight exposure (Kieber et al., 2012; Lee et al., 2013; McKnight et al., 2001; Murphy et al., 2013; Cory and McKnight, 2005; Korak et al., 2014; Chin et al., 1994). The specific impacts are summarized. (1) Changes in optical characteristics. Sunlight exposure can cause the photo-bleaching of COM. Previous studies shown that chromophores produced by wood-burning were significantly photo-bleached in aerosols (Lee et al., 2014; Zhong and Jang, 2014). Yet the mechanisms of photo-bleaching process are still not complete clear. (2) Changes in chemical composition. Photochemistry have a significant effect on the composition of COM, because photolysis cause that COM decompose into small molecules. Therefore, COM may have lower volatility and higher oxidation degree after photolysis (Vodacek et al., 1997; Del Vecchio and Blough, 2002; Gonsior et al., 2009; Grieshop et al., 2009). In contrast, COM could also be generated due to photochemical reaction. For example, oligomeric COM could be generated by a mixture of anthracene and naphthalene suspensions due to self-oxidation under light conditions; photo-oxidation of aromatic isoprene oxides are an important source of high-molecular-weight COM (Altieri et al., 2006; Altieri et al., 2008; Haynes et al., 2019; Holmes and Petrucci, 2006; Perri et al., 2009). Changes in chemical composition affect photochemical activity in turn. Therefore, it is crucial to illustrate the changes in optical characteristics and chemical composition, which could promote understanding the characteristic and mechanisms of COM photochemistry in aerosols.

Atmospheric COM not only decompose and transform, but also participate in the complex photochemical reaction, which further affect the aerosol aging (Malley et al., 2017). On the one hand, COM could participate in atmospheric photochemical processes directly. For example, excited COM react with organic matters and promote secondary organic aerosols (Zhao et al., 2015; Saleh et al., 2013; Zhong and Jang, 2014; Lee et al., 2014; Liu et al., 2016). Various secondary photochemical processes also increase the complexity of COM composition (Wenk et al., 2011; Zhou et al., 2019; Smith et al., 2014; Richards-Henderson et al., 2015; Kaur and Anastasio, 2018; Chen et al., 2016a and b). On the other hand, COM also participate in atmospheric photochemical reactions indirectly because COM can induce reactive species. Powers et al. (2015) probed the photochemical activity of the deep ocean refractory dissolved organic carbon (DOC) through simultaneous measuring the rates of both H_2O_2 and O_2^- photoproduction in the laboratory.

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Photochemical activity is universal feature of DOC. For example, aromatic ketones could be excited to generate triplet state (^{3}COM*) under light conditions (Rosario-Ortiz and Canonica, 2016; Del Vecchio and Blough, 2004; Wenk et al., 2013; Ma et al., 2010). ^{3}COM* induce reactive oxygen species (ROS), such as singlet oxygen ($^1O_2$), super-oxygen ($\bullet O_2^-$) and hydroxyl (•OH), which could drive aerosol aging (Paul Hansard et al., 2010; Szymczak and Waite, 1988; Zhang et al., 2014; Rosario-Ortiz and Canonica, 2016; Sharpless, 2012; Haag and Gassman, 1984). COM have the potential effects on aerosol aging, so it is necessary to clarify the path of COM driving aerosol aging.

In order to illustrate the effect of COM photo-degradation on the optical properties and photochemical reactivity in aerosols, we simulate the photolysis process of primary organic aerosol (POA) and ambient particle matter (ambient PM) in laboratory. The characteristics of photo-degradation in water-soluble and water-insoluble chromophores are clarified by the approach of excitation-emission matrices (EEM) combined with parallel factor analysis (PARAFAC). The effects of aerosol aging on photochemical reactivity (photochemical reactivity is characterized by triplet state and singlet oxygen generation capacity) are also stated by reactive species capture technology and electron paramagnetic resonance spectrometer (EPR).

2. Experimental Section

2.1 Sample Collection

A total of 16 samples were collected (The details of the samples are shown in Table S1 of SI). The ambient PM samples were collected in Shaanxi University of Science and Technology, Xi'an, Shaanxi Province (N34°22′35.07″, E108°58′34.58″; the sampling device is about 30 m from the ground). The ambient PM samples were collected on a quartz fiber filter (Pall life sciences, Pall Corporation, America) by an intelligent large-flow sampler (Xintuo XT-1025, Shanghai, China) with a sampling time of 23 h 30 min and a sampling flow rate of 1000 L/min. The ambient PM samples were stored in the refrigerator at -20 ℃ prior to use.

The POA samples were collected through a combustion chamber. Wheat straw, corn straw, rice straw and wood were burned at about 500 ℃ in the tube stove. The clean air was introduced at a flow rate of 2 L/min to ensure complete combustion. The particle matters entered the collected chamber. The clean air was introduced into the collected chamber at a flow rate of 2 m^3/h to dilute the combustion gas. POA samples were collected on the quartz fiber filter (Pall life sciences, Pall Corporation, America) with a diameter of 37 mm. The POA sample were stored in the refrigerator at -20 ℃ prior to use.

2.2 Photolysis experiment

A high-purity quartz reactor was designed for the photolysis experiment (**Fig.1a**). A rubber gasket was embedded on the upper edge of the reactor. The reactor was clamped with a high-purity quartz cover to form a sealed environment. Two vents were designed in the low position of the reactor. The vents were connected to water circulator to ensure that the temperature was about 25°C in the reactor. The reactor was placed on a magnetic stirrer and the rotation speed was 200 rmp to stabilize the temperature and humidity (~50%). A xenon lamp was equipped with a VISREF light

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filter (PLS-SXE 300, Perfectlight, China) to simulate sunlight (The wavelength spectrum of the xenon lamp is shown in Figure S1 of SI). The light intensity per unit area was about 1.2-1.3 times the solar light at 12:00, at N34°22′35.07″, E108°58′34.58″. A support was placed in the reactor and the samples were placed on the support. The illumination time were 0 h, 2 h, 6 h, 12 h, 24 h, 3 d and 7 d, respectively.

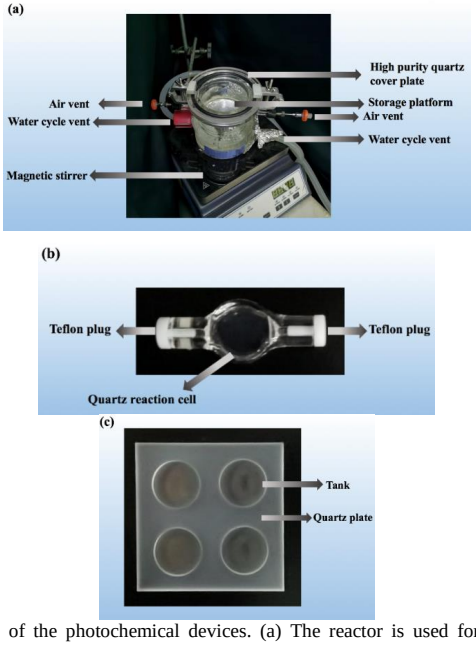

Fig.1 Schematic diagrams of the photochemical devices. (a) The reactor is used for maintaining the reaction environment. The water cycle vents are connected with a water circulator to maintain the temperature. (b) The reactor is used for triplet state experiments. The reactor is made of quartz. The plugs are made of Teflon. The internal volume is 200 μL. (c) A reactor is used for the experiment of triplet state inducing singlet oxygen. The size of quartz plate is 35×35 mm^2. The size of the tanks is a radius of 5.6 mm and a depth of 2.5 mm.

2.3 Sample extraction

The samples extracts were obtained by the approach of ultrasonic extraction. The original and photolyzed samples were extracted with ultra-pure water (>18.2 MΩ•cm, Master series, Hitech, China) and the suspensions were filtered through a 0.45 μm filter (Jinteng, China) to obtain the water-soluble organic matter (WSOM). After water extraction, the samples were further extracted with methanol (HPLC Grade, Fisher Chemical, America) to obtain water-insoluble organic matter (WISOM) using the above method. The blank samples were also extracted. The specific extraction method was the same as sample extraction, which was used to correct the effect of the background.

2.4 OC/EC analysis

The method of organic carbon (OC) analysis could refer to the previous literature (Mu et al., 2019). Briefly, 100 μL of extracts were injected on the clean quartz filter. Then, the filters were dried out with a rotary evaporator. Carbonaceous components were analyzed by the OC/EC online

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analyzer (Model 4, Sunset, America) with the approach of NIOSH 870 protocol (Karanasiou et al., 2015). Six parallel samples were analyzed and the results showed that the uncertainty of the method was <3.7% (one standard deviation).

2.5 Optical analysis

The light absorption and EEM spectra of the extracts were analyzed by an Aqualog fluorescence spectrophotometer (Horiba Scientific, America). The extracts were diluted for optical analysis (The concentrations are shown in Table S2 of SI). The absorption spectra were recorded in the wavelength range of 200-600 nm. The range of excitation wavelength was 200-600 nm and the range of excitation wavelength was 250-800 nm. The interval was 5 nm. The exposure time was 0.5 s. The background samples were also analyzed using the same method and the background signals were subtracted from the sample signals.

The EEM data was analyzed by the PARAFAC model to identify chromophores (The detailed analysis process refer to the previous papers) (Chen et al., 2016b; Chen et al., 2016a). Briefly, according to the EEM characteristics and the residual error variation trend of the 2-7 component PARAFAC models, 4 component PARAFAC model was selected (Analysis error of the models are shown in Figure S2 of SI).

2.6 Triplet state generation experiment

The triplet states generation ability before and after photolysis were studied. Chemical probe 2,4,6-trimethylphenol (TMP) was used as the capturing agent for the triplet state. 60 μL of WSOM extracts (OC concentrations are shown in Table S3) and 60 μL of TMP solution (c_{TMP} = 20 μM, Aladdin, China) were mixed in the cell (**Fig.1b**). The cell was placed in the reactor (**Fig.1a**) and the reaction conditions were the same as shown in 2.2. The illumination time was 0, 5, 10, 15, 30, 45, 60 and 90 min, respectively. 90 μL mixed solution was taken out from the cell at different time points. Then 30 μL of phenol solution (c_{phenol} = 50 μM, Aladdin, China) were added into the mixed solution (Phenol solution was used as the internal standard substance for TMP quantification). TMP was quantified by liquid chromatography (LC).

The analyzed parameters of LC are as follows: C18 column (Xuanmei, China); mobile phase: acetonitrile/water = 1/1 (v/v); flow rate: 1 mL/min; UV detector: detection wavelength 210 nm. Kaur and Anastasio (2018) and Richards-Henderson et al. (2015) have found that TMP consumption conform to first-order kinetics in the triplet state capture reaction. The first-order kinetic equation was used to fit exponential relationship among the TMP concentration (c_{TMP}/μM), the illumination time (t/min) and triplet state generation rate constants (k_{TMP}/min^{-1}):

$$c_{TMP} = a \cdot e^{k_{TMP} \times t} \quad (1)$$

2.7 Triplet state driving singlet oxygen experiment

The effects of the photolysis on singlet oxygen in aerosols were studied. 4-Hydroxy-2, 2, 6, 6-tetramethylpiperidine (TEMP, c_{TEMP}=240 mM, Aladdin, China) was used as the capturing agent of singlet oxygen and captured singlet oxygen was quantified by EPR spectrometer (MS5000, Freiberg, Germany). Sorbic acid (SA, C_{SA}=133.3 μM, Aladdin, China) was used as quenching agent for triplet

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state. The method was as follows: (1) 40 μL WSOM, 40 μL TEMP and 40 μL ultra-pure water were mixed in the tanks (**Fig.1c**). The mixed solution was placed in the reactor (**Fig.1a**). Then, 50 μL of the mixed solution was taken out by capillary for EPR analysis; (2) 40 μL of WSOM, 40 μL of TEMP and 40 μL of ultra-pure water were mixed. The mixed solution was placed in the reactor for 60 min without illumination. Then 50 μL of the mixed solution was taken out by capillary for EPR analysis; (3) 40 μL of WSOM, 40 μL of TEMP and 40 μL of ultra-pure water were mixed in the cell. The mixed solution was placed in the reactor for 60 min with illumination. 50 μL of the mixed solution was taken out by capillary for EPR analysis; (4) 40 μL of WSOM, 40 μL of TEMP and 40 μL of SA solution were mixed in the cell. The mixed solution was placed in the reactor for 60 min with illumination, then 50 μL of the mixed solution was taken out by capillary for EPR analysis.

3. Results and discussion

3.1 Effect of COM photo-degradation on carbonaceous components

Organic matters can be decomposed and transformed in aerosol due to illumination (Wong et al., 2015). **Fig.2** describe the variable characteristics of total organic carbon and carbonaceous components before and after COM photolysis. The results show that both water-soluble and water-insoluble organic matter partially photolysis in POA samples (**Fig.2A**), with an average decrease of 22.1% and 3.5%, respectively. Compared with POA, WISOC decompose obviously in ambient PM, with an average decrease of 26.3%, while the WSOC do not change significantly (**Fig.2B**).

Photolysis also result in the variation on carbonaceous components. In POA samples (**Fig.2A**), the relative content of the OC1 (OC1 and OC2-4 are the different stage in the process of thermal-optical analysis) decrease, which is the main loss of OC. The organic matters in the OC1 stage are characterized by small molecular weight and highly volatile (Karanasiou et al., 2015). The result shows that OC1 has a stronger ability of photo-decompose. On the other hand, the pyrolysis carbon (OPC) in WISOM show an increasing trend (an average increase of 2.4 times). Generally, the pyrolysis carbon is oxygen-containing substance. Thus, the increase of oxygen-containing organics may be due to the aerosols aging. Contrast with POA, the carbonaceous components are relatively stable in ambient PM (**Fig.2B**). The result reflect that ambient PM samples have been subjected to sufficient atmospheric oxidation, so organic matters are not decomposed or oxidized again.

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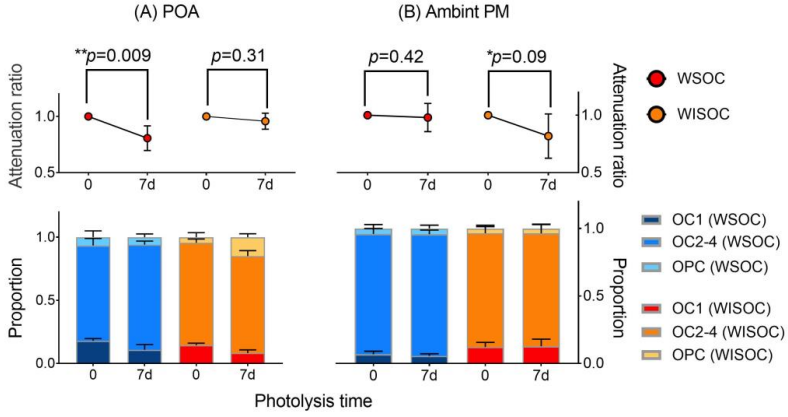

Fig.2 Variations of total carbon and carbonaceous components before and after photolysis. The *p*-value is the probability that two sets of data have the same level (two-tailed test). * and ** are represent the significant difference at the 0.1 and 0.01 levels, respectively.

3.2 Effect of COM photo-degradation on optical properties

Both absorbance and total fluorescence volume (TFV, RU-nm^2/m^3) represent an obvious decreasing trend due to aerosol photolysis (**Fig.3**). Changes in optical properties are shown in Figure S3, S4 and S5. The decrease of absorbance confirm that COM are photo-bleached (Duarte et al., 2005). The subduction function of photolysis on absorbance is significant (Aiona et al., 2018). In POA (**Fig.3B**), TFV decrease by 74.8% on average and the attenuation characteristics of water-soluble and water-insoluble components are similar. The attenuation of fluorescence intensities is different from Aiona's paper (Aiona et al., 2018). Changes in fluorescence intensities may depend on the types of COM and the photochemical environment. Exceptionally, the water-insoluble component of wood burning only decrease by 9.0% (Figure S5), which is significantly different from other POA samples. The characteristics of TFV and WISOC of wood burning (section 3.1) are similar, which probably attribute to the slight generation of secondary water-insoluble organic substances. The characteristics of TFV attenuation in ambient PM (rate constant k = 0.04 h^{-1}) is different from POA (k = 0.07 h^{-1}). Compared with water-soluble chromophores, the water-insoluble chromophores photo-decompose obviously and the TFV decrease by 79.1%. In contrast, changes in the water-soluble chromophores are only 21.9% on average, while 48.8% in POA samples. The low attenuation result from COM have undergone a long-term atmospheric aging process and the water-soluble COM are easier to photolysis.

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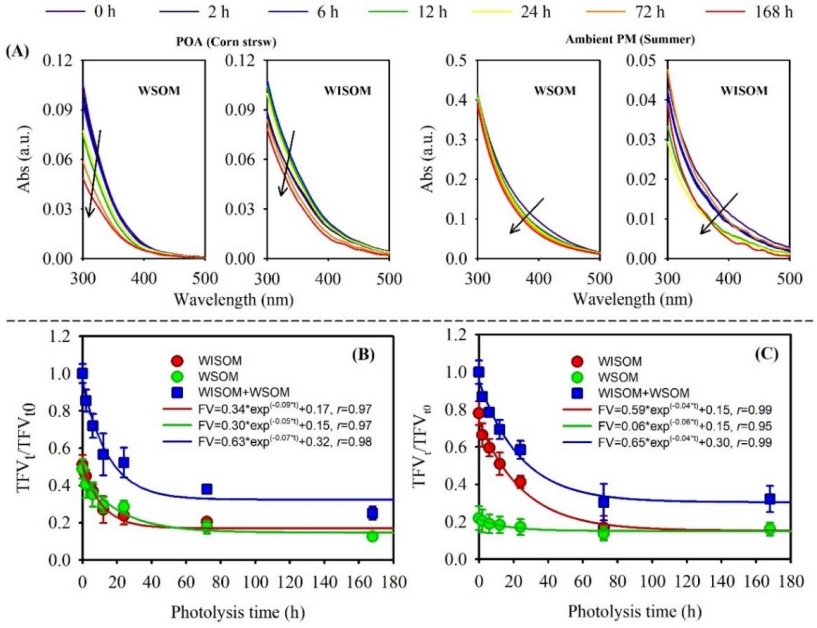

Fig.3 The changes of light absorption and fluorescence volume in the photolysis process. (A) The light absorption spectrum. (B) and (C) show the attenuation curve of average fluorescence volume of POA (except for the wood sample) and ambient PM samples, respectively.

Four types of COM are identified by the approach of EEMs-PARAFAC and the composition variations are studied (**Fig.4A**). The fluorescence peaks of C1 and C2 appear at (Ex./Em. = 224/434 nm) and (Ex./Em. = 245/402 nm), and the characteristics are similar to high and low oxidation HULIS, respectively (Chen et al., 2016b; Birdwell and Engel, 2010). The peaks of C3 and C4 appear at (Ex./Em. = 220/354 nm) and (Ex./Em. = 277/329 nm) and these two chromophores were identified as protein-like organic matters (PLOM-1 and PLOM-2) in previous studies (Sierra et al., 2005; Huguet et al., 2009; Chen et al., 2016a and 2016b; Coble, 2007; Fellman et al., 2009).

The compositions of chromophores change significantly in the photolysis process. In POA (**Fig.4B**), the high-oxidation HULIS show an obvious increasing trend in water-soluble component and the relative content increase by 25.7% on average. On the contrary, low oxidation HULIS and PLOM show a decreasing trend and the relative attenuation are 6.0% and 19.7%, respectively. The proportion variation indicate that high-oxidation HULIS chromophores could be generated in the photochemistry process and low oxidation HULIS and PLOM chromophores may be photolyzed (Tang et al., 2020; Chen et al., 2020). Not only in water-soluble chromophores, the content of high-oxidation HULIS also increase in water-insoluble chromophores (average 17.5%). Low-oxidation HULIS also decrease in water-insoluble chromophores. In ambient PM, the content of high-oxidation HULIS increase and the low-oxidation HULIS decrease (**Fig.4C**), which reveal that low-oxidation HULIS could be transformed into high-oxidation HULIS in aerosol aging process (Chen et al., 2016a). Thus, high-oxidation HULIS could be used to trace the aerosols aging degree.

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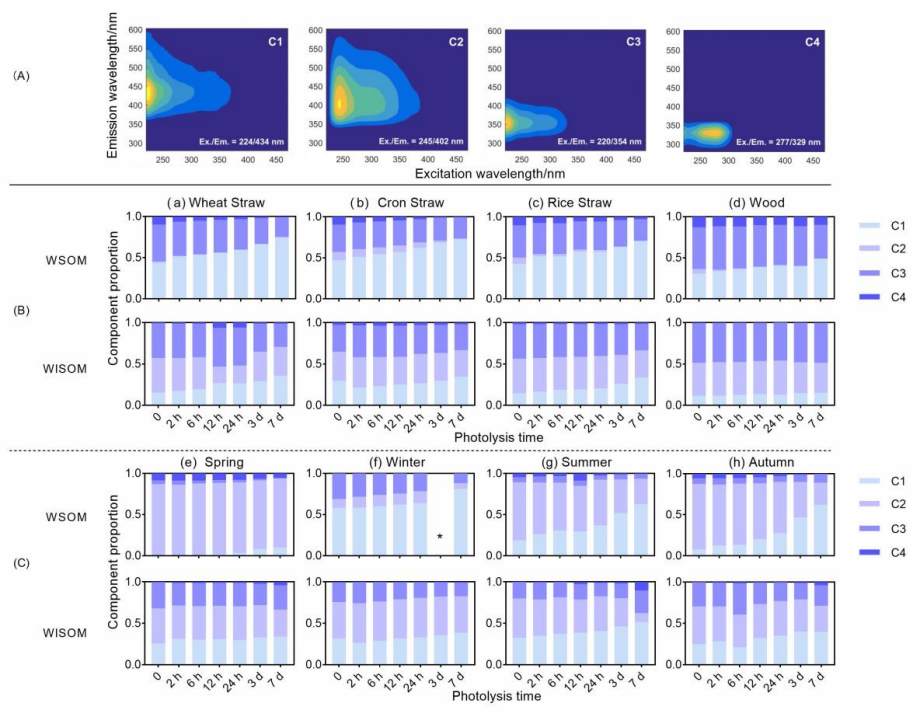

Fig.4 (A) The EEM spectra of chromophores; (B) is the variation characteristics of chromophores in POA; (C) is the variation characteristics of chromophores in ambient PM. *: The data of 3-day photolysis of water-soluble chromophores in winter is unavailable.

3.3 Effect of COM photo-degradation on aerosol photochemical reactivity

COM photo-degradation has a significant effect on aerosol photochemical reactivity. The photochemical activity is characterized by triplet state and singlet oxygen. **Fig.5** show the difference of triplet state generation capability before and after the photolysis (Details are shown in Figure S6 of SI). The generation rate of triplet state is decreased by 11% on average after COM photolysis in ambient PM, while statistical analysis show that photo-degradation do not significant affect the triplet state generation (p = 0.38, two-tailed test). On the contrary, the triplet states generation rate markedly increases by 75% on average in POA (p = 0.07, two-tailed test), which indicate that COM photo-degradation has a significant improvement effect on triplet state generation. COM are photo-decomposed, while the triplet state generation ability remains unchanged or increase. The results are not as expected. However, the result can be explained by recent study (Chen et al. 2020 for ACPD): only a small number of chromophores have the ability to generate triplet states in aerosols. The decomposition of most chromophores do not represent the decomposition of these specific types of chromophores. We use a high concentration of TMP, in this case, TMP mainly capture short-lived triplet state (Rosado-Lausell et al., 2013). Thus, chromophores that can form a short-lived triplet state may not be reduced or even generated during the photolysis process.

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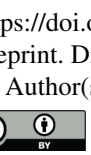

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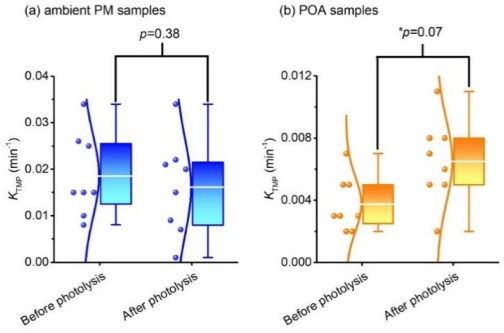

Fig.5 The changes of the triplet state generation capacity in (a) the ambient PM and (b) POA samples before and after photolysis. The line from bottom to top in the box plots are minimum, first quartile, the average value (white lines), third quartile, and maximum, respectively. The *p*-value is the probability that two sets of data have the same level (two-tailed test). * represents a significant difference at the 0.1 level.

COM can generate triplet states and further induce singlet oxygen (McNeill and Canonica, 2016). The effects of COM photo-degradation on singlet oxygen are illustrated through the approach of chemical capture and EPR analysis. Typical EPRs spectra of $^1O_2$ are shown in **Fig.6** (EPR spectra of all samples are shown in Figure S7 and Figure S8). More narrowly, in the original POA samples (i.e. the sample with photolysis time is 0, details of samples are described in section 2.2), there is no significant $^1O_2$ signal before light excitation (the red curve in **Fig.6A (I)**) and only a small amount of $^1O_2$ is generated after 60 min in dark (the red curve in **Fig.6A (II)**), which indicated that POA has certain oxidability. As expected, compared with the sample without light excitation (the red curve in **Fig. 6A (I)**), the signal intensity of $^1O_2$ increase by 3 times after 60 minutes of light excitation (the red curve in **Fig. 6A (III)**), which prove the significant promoting effect of light on $^1O_2$. However, $^1O_2$ is not reduced when the triplet state is quenched by sorbic acid (the red curve in **Fig.6A (IV)**). Sorbic acid is a trapping agent of high-energy triplet state (triplet energies E_T = 239-247 kJ/mol) (Zhou et al., 2019; Moor et al., 2019), therefore, the above results indicate that the low-energy ^{3}COM* (E_T <239 kJ/mol) may be the main precursor for $^1O_2$ (E_T = 94 kJ/mol) in POA.

The COM photo-degradation can change the yield of $^1O_2$. Compared with original POA samples, the signal intensity of $^1O_2$ decrease significantly in the samples with 7 days of photolysis (the blue curve in **Fig.6A**), with an average decrease of 42.1% (**Fig.6C**), which prove that photo-degradation has a restraining effect on the photochemical activity in POA. Similar to the original sample, the signal intensity of $^1O_2$ do not decrease obviously when the high-energy triplet states are quenched by sorbic acid in the photolyzed samples. The mechanism is same as original samples. The results also reveal that the COM photo-degradation process do not change the mechanism of low-energy ^{3}COM* inducing $^1O_2$ in POA.

The photochemical characteristics of ambient PM are different from POA. More narrowly, there is no obvious $^1O_2$ signal in original ambient PM samples before light excitation (the red curve in **Fig.6B (I)**). $^1O_2$ is also not generated after 60 min in dark (the red curve in **Fig.6B (II)**). The content of $^1O_2$ increase significantly after 60 minutes of light excitation (the red curve in **Fig.6B**

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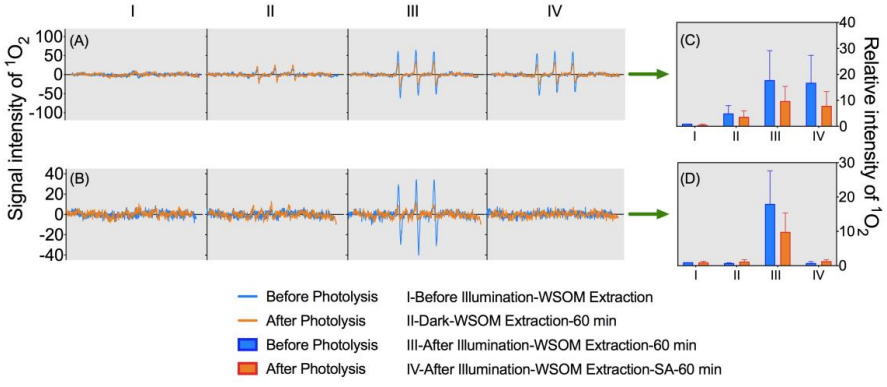
285 **(III)**). When the triplet states are quenched by sorbic acid (**Fig.6B(IV)**), the signal of $^1O_2$ disappear.
286 The result suggests that $^1O_2$ is mainly induced by high-energy ^{3}COM* in ambient PM. Compared
287 with the original samples, the signal intensity of $^1O_2$ decrease by 41.0% on average in photolyzed
288 samples (the red curve in **Fig.6B**). This characteristic reveal the restraining effect of COM photo-
289 degradation on photochemical activity in ambient PM. The restraining effect is similar to POA.
290 However, the quenching effect of sorbic acid on various aerosols are different (**Fig.6 (IV)**). The
291 above results directly prove that the precursor of high-energy triplet states could be photolyzed,
292 which directly lead to the decrease of $^1O_2$ yield in the ambient PM. Other experiments are needed
293 to prove whether the low-energy triplet precursors in POA are photolyzed and cause a decrease in
294 the yield of $^1O_2$.



295
296 **Fig.6** Variations of DOM inducing $^1O_2$ before and after photolysis. (A) and (C) are the results obtained from POA
297 samples. (B) and (D) are the results obtained from Ambient PM. The left of the figure was the EPR spectra of $^1O_2$.
298 The right of the figure was the content variations of $^1O_2$. Relative content was calculated with a standard of the signal
299 intensity of $^1O_2$. The standard is the signal intensity of $^1O_2$, which is induced by un-photolyzed and un-illuminated
300 samples.

301 ## 4. Implication

302 The characteristics of COM photo-degradation and the effects of photo-degradation on the
303 photochemical activity in different aerosols are studied. Firstly, we prove that the photo-degradation
304 could lead to COM decompose and change in types. The conversion process of low-oxidation
305 HULIS to high-oxidation HULIS is observed in ambient PM, which reflect the significant influence
306 of photo-degradation on chemical composition. In turn, the attenuation and type conversion of COM
307 provide an important basis to trace the aerosol aging process. Optical properties are also effected by
308 COM photo-degradation. Secondly, we evaluate the effect of COM photo-degradation the
309 photochemical activity. Triplet state generation ability remain unchanged or increased in the aerosol
310 aging process, while photo-degradation has a significant restraining effect on the $^1O_2$ yield. So
311 photolysis and/or conversion of COM could be considered to be the main influence factor for
312 photochemical reaction capacity. In addition, the photochemical reaction mechanisms and aerosol
313 aging processes are relatively different in aerosols. It may be more useful to distinguish the types

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of ^{3}COM* into high and low energies, so that the mechanism of COM photochemical reaction can be elucidated. In summary, the aerosol aging process has a remarkable impact on atmospheric photochemistry. Aerosol aging can not only change the type and content of COM, but also change their photochemical activity, which furtherly has a potential impact on the aerosol fate. Different types of aerosols have different aging mechanisms, so the environmental impacts caused by COM should also be different.

Data availability. All data that support the findings of this study are available in this article and its Supplement or from the corresponding author on request.

Supporting information. Additional details, including Tables S1−S3, Figures S1−S8, calculation of optical characteristics of WSOM/WISOM, are contained in the SI.

Author contributions. QC and ZM designed the experiments and data analysis. ZM and LZ performed sample collection. ZM performed the photochemical experiment. ZM and DG performed the OC/EC analysis and optical analysis. HL performed the EPR analysis. QC prepared the paper with the contributions from all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

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